

The Adsorption of hydrocarbons on model multilayer mirror surfaces: $\text{TiO}_2(011)$, $\text{Ru}(10\bar{1}0)$ and Al_2O_3 films

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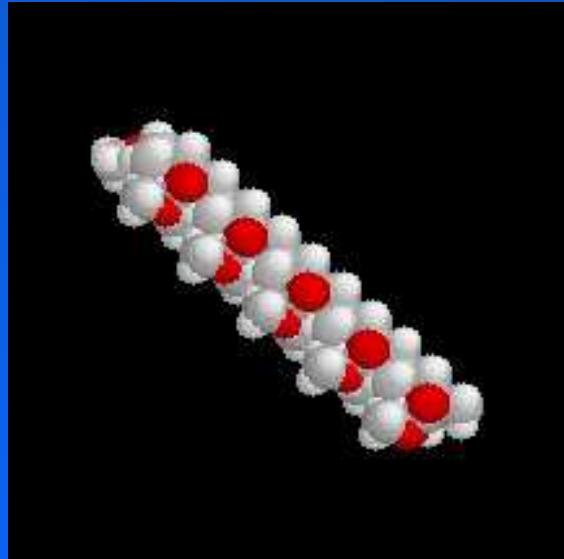
Objective

Determine adsorption properties, as well as thermal- and electron-induced decomposition, of the hydrocarbons MMA, benzene, toluene, isobutylene, ..., on the single crystal $\text{TiO}_2(011)$, Ru(10-10) and thin film Al_2O_3 surfaces as model MLM capping layers

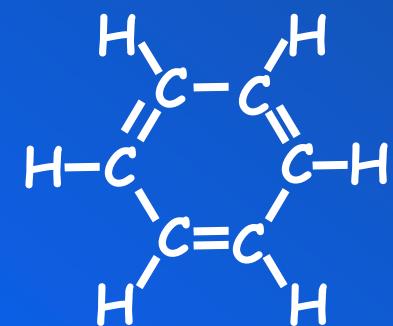
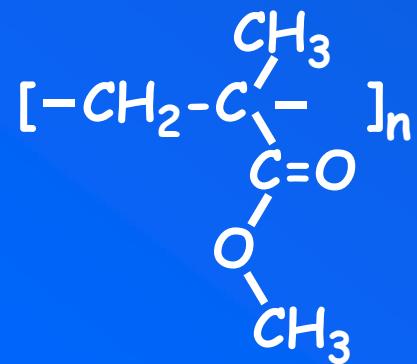


Molecules studied

methyl methacrylate (MMA)



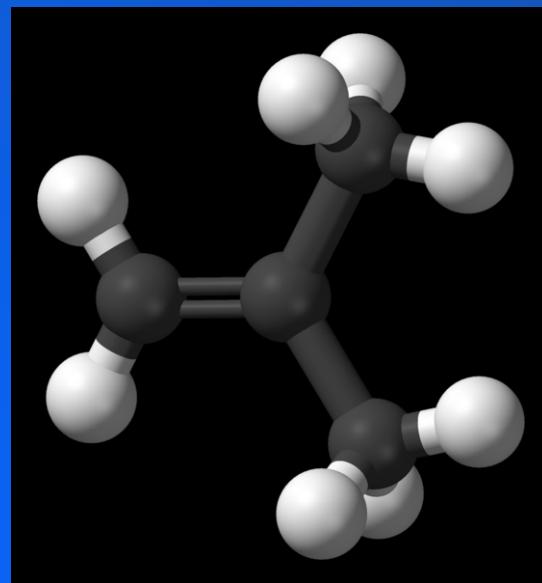
benzene



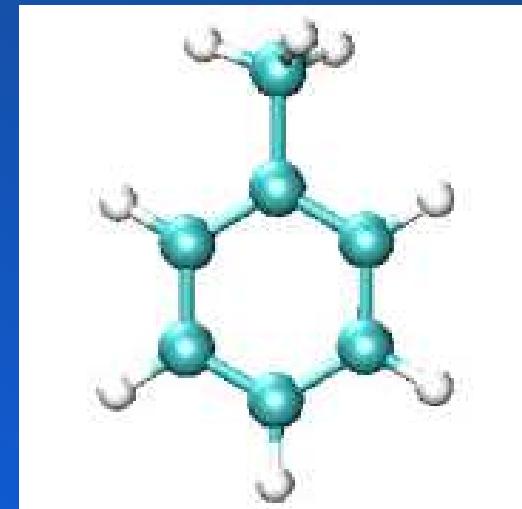


Molecules studied

isobutylene

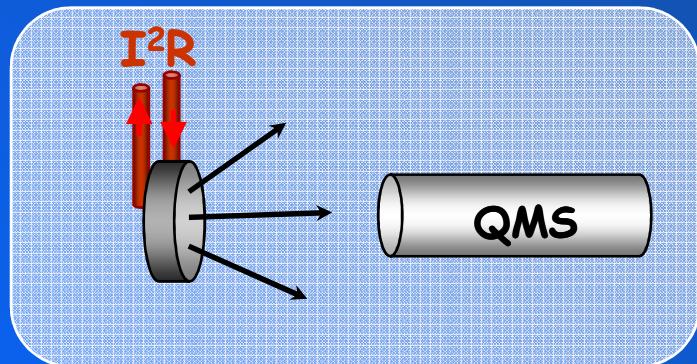


toluene



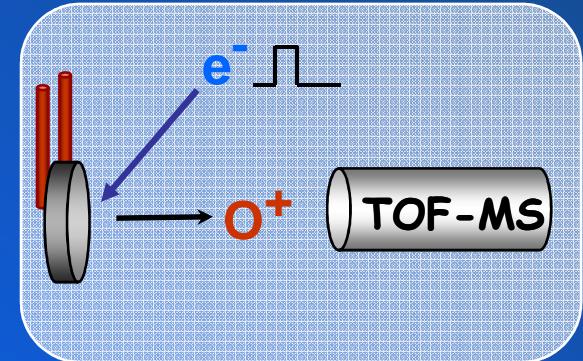
Methods

TPD: Temperature Programmed Desorption



- *clean surface
- *dose gas (MMA, C_6H_6)
- *heat at linear rate
- *determine energies, lifetimes

ESD: Electron stimulated desorption and reaction



XPS: X-ray photoelectron spectroscopy

LEIS: Low energy ion scattering

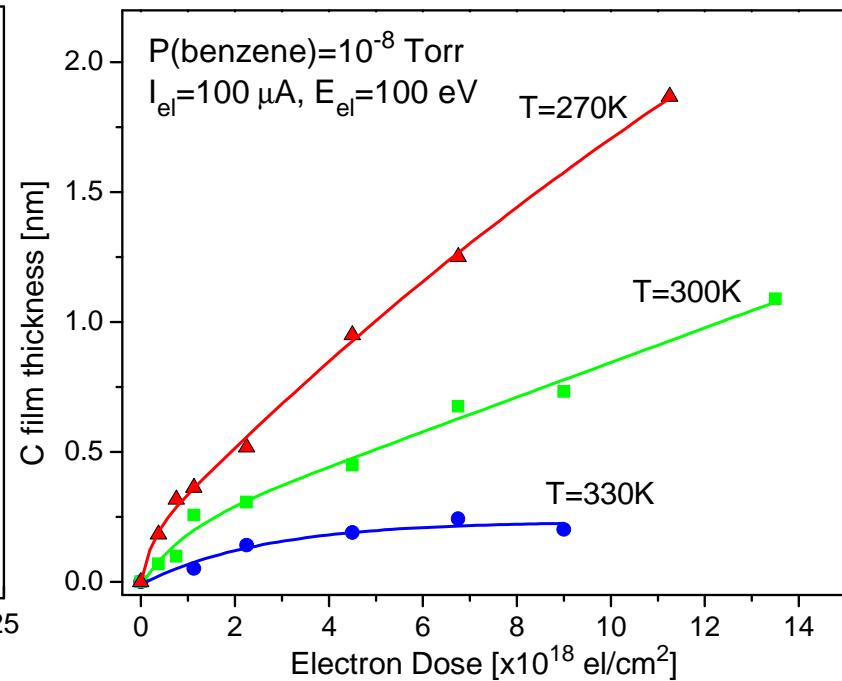
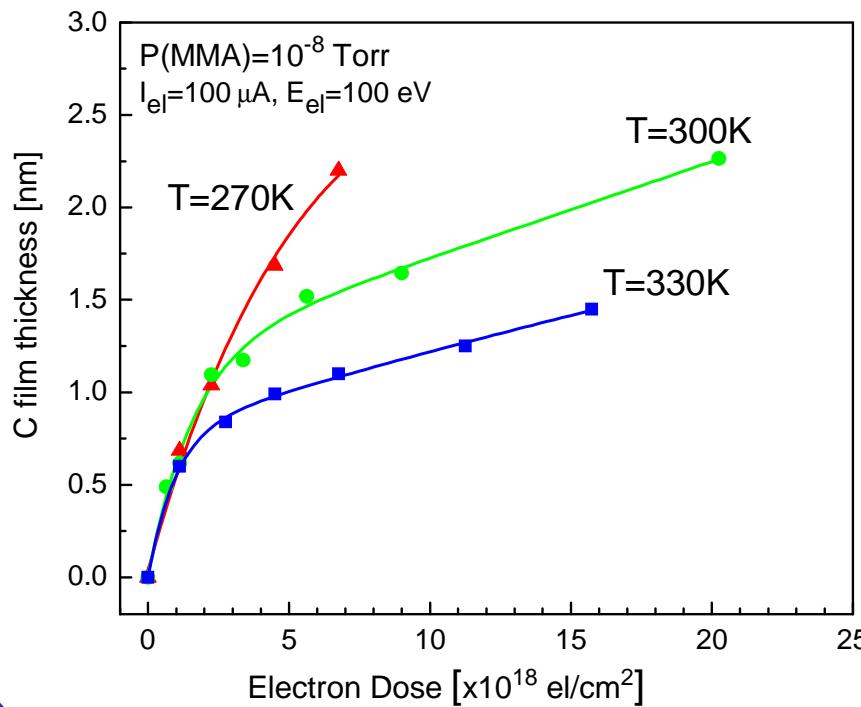
Secondary electron yield (synchrotron radiation)



C growth on TiO_2 under electron irradiation in MMA and benzene vapor: effects of substrate temperature

MMA

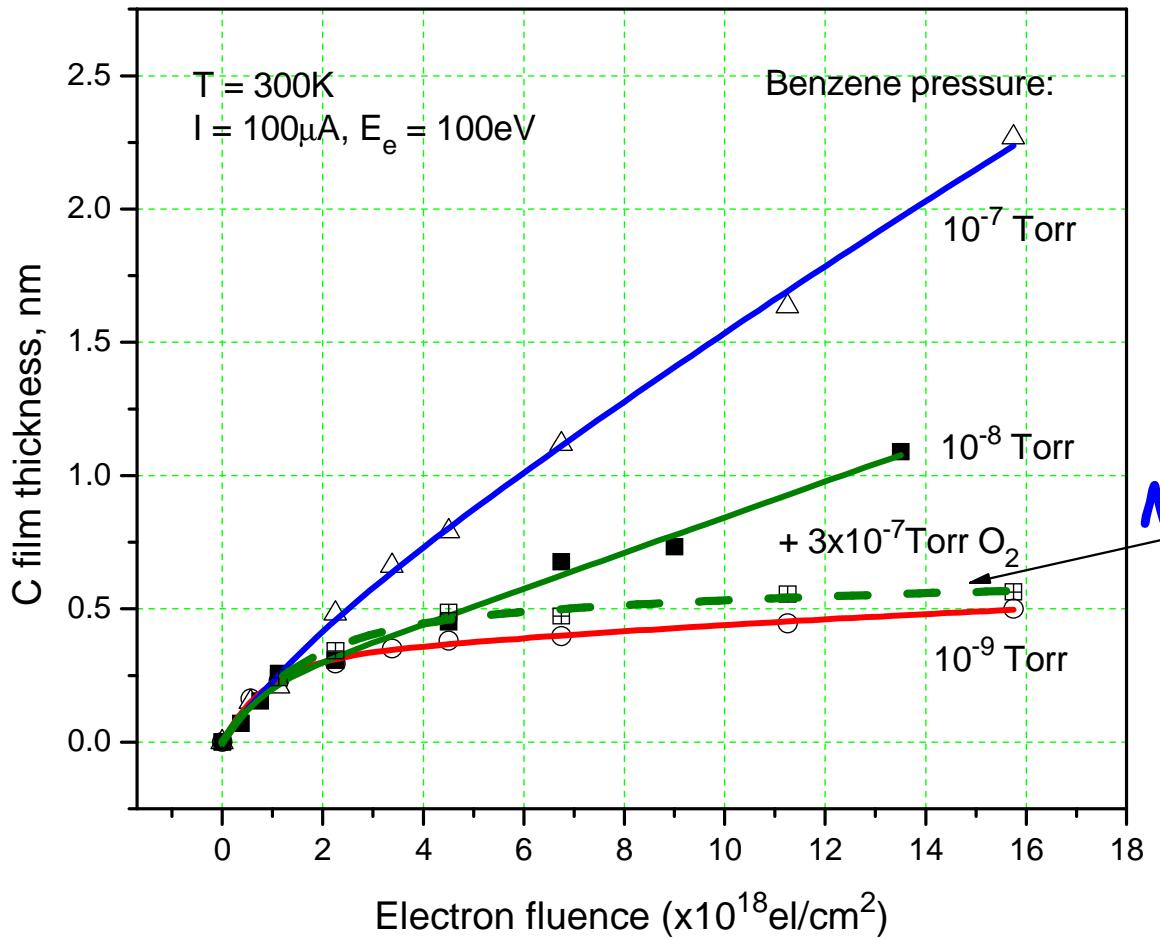
benzene



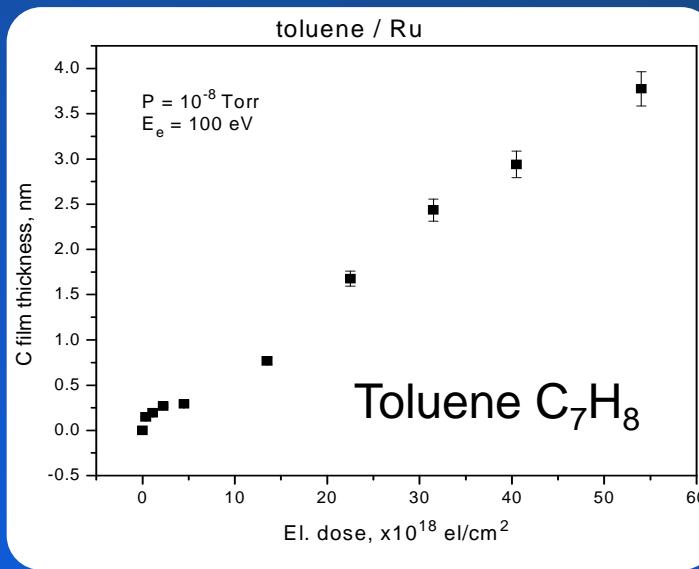
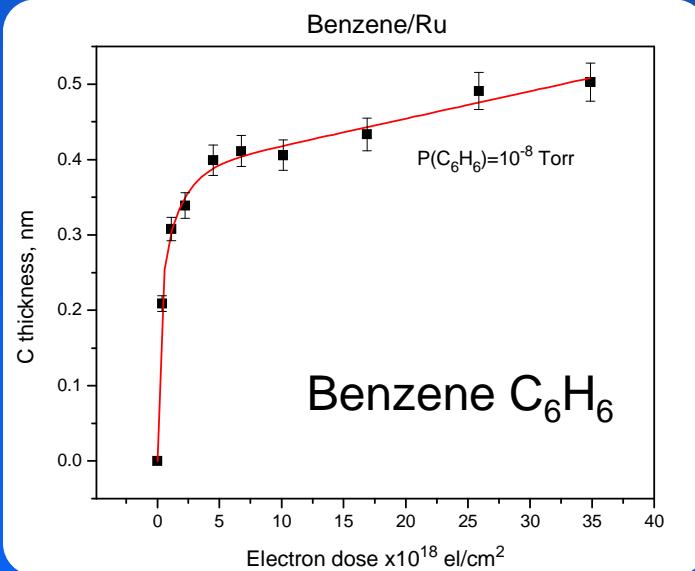
- Growth rate is higher on clean surface than on C-covered
- Increasing substrate T lowers C growth rate \rightarrow lower molecule residence time on surface
- C growth from MMA $\sim x2$ than from benzene



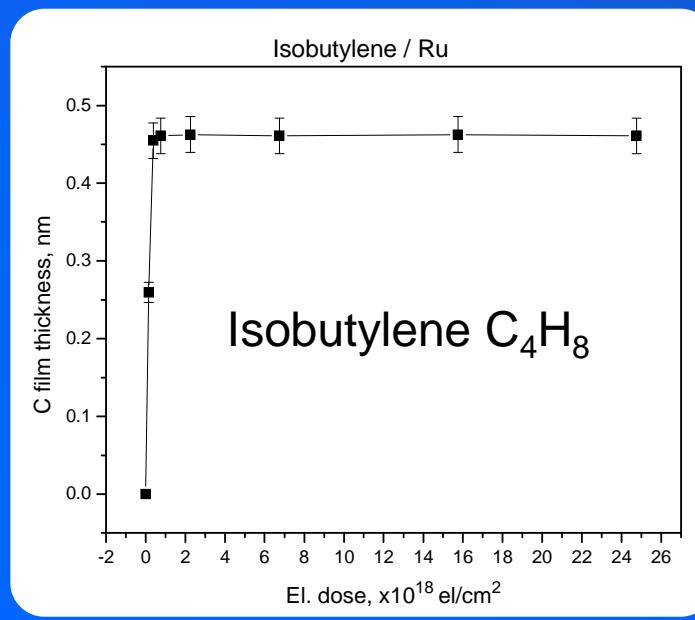
C growth on TiO_2 under electron irradiation: effects of benzene pressure; mitigation in O_2



Electron-irradiation-induced C accumulation on Ru in the presence of hydrocarbon vapor



Pressure $\sim 10^{-8}$ Torr
T=300 K
Elect. energy 100 eV

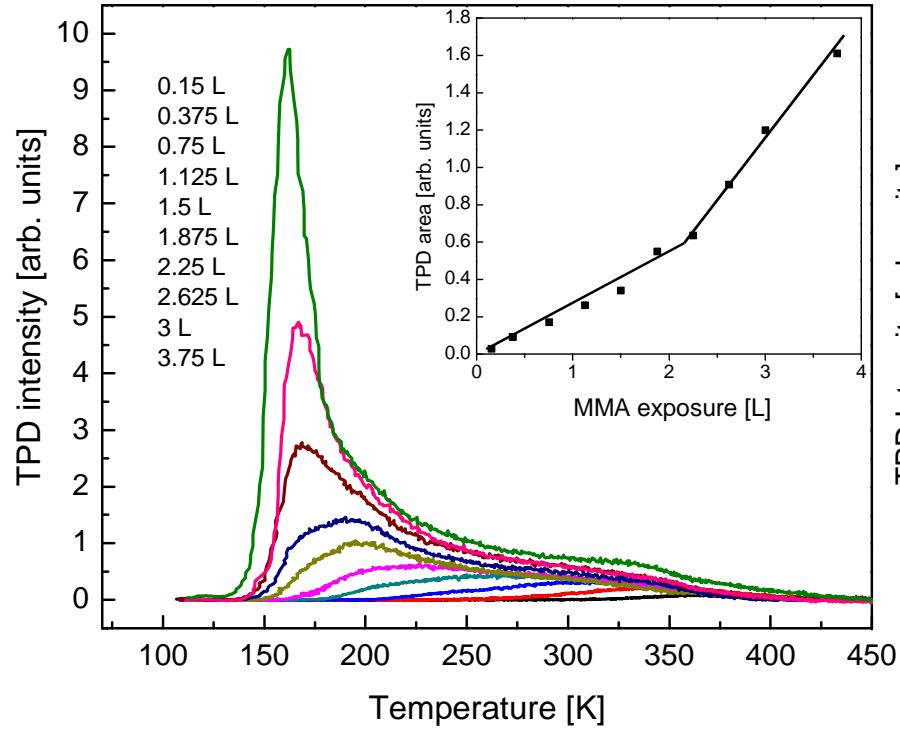


- Rapid C accumulation on Ru surface
- TOLUENE: significant C accumulation on C
- ISOBUTYLENE: No C accumulation on C

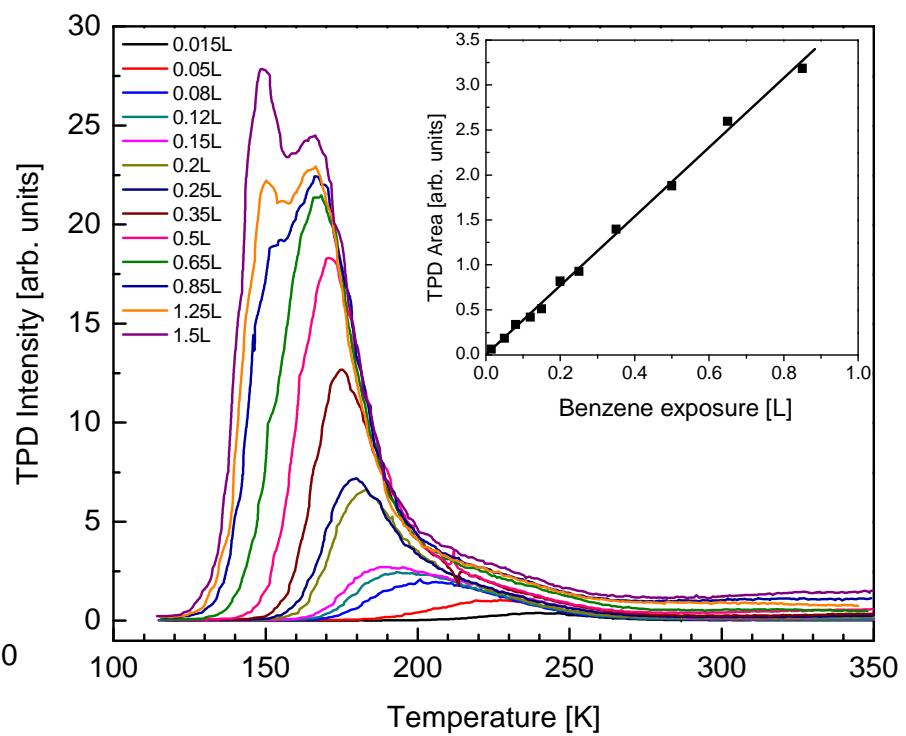


Temperature Programmed Desorption (TPD) of MMA and C_6H_6 from clean $TiO_2(011)$

MMA



benzene

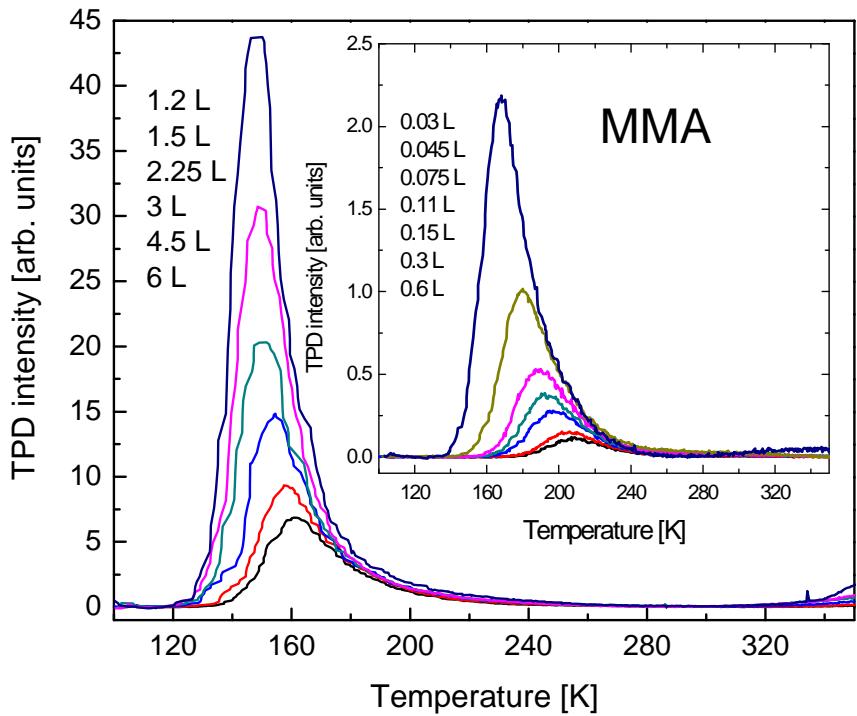


- Adsorption energy decreases with increasing coverage
- Partial dissociation of MMA on TiO_2 on defects ($\sim 0.1\text{ML}$)
- No carbon accumulation from benzene

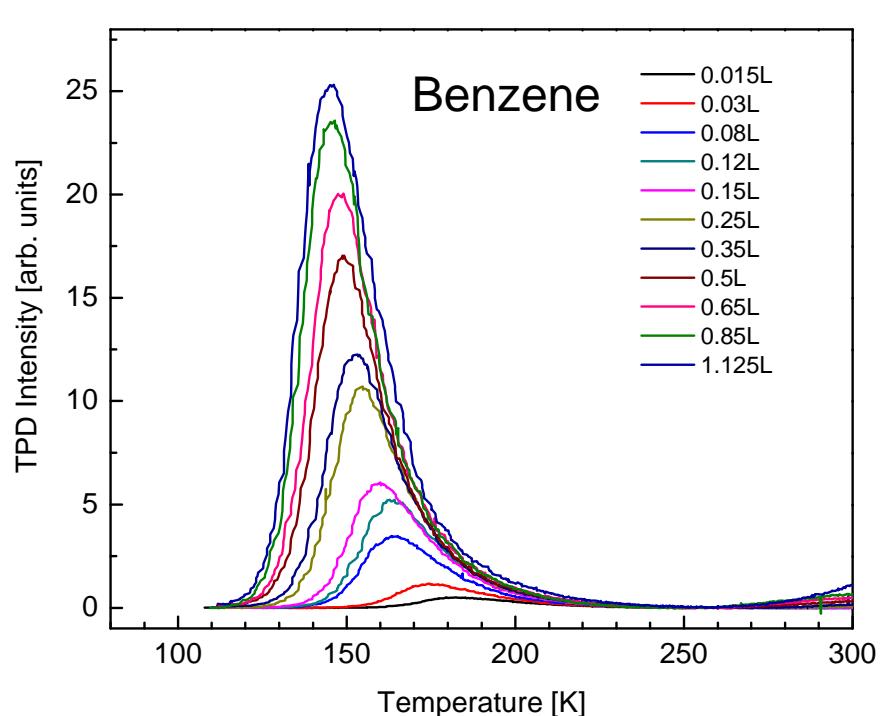


Temperature Programmed Desorption (TPD) of MMA and C₆H₆ from 2nm C-covered TiO₂(011)

MMA



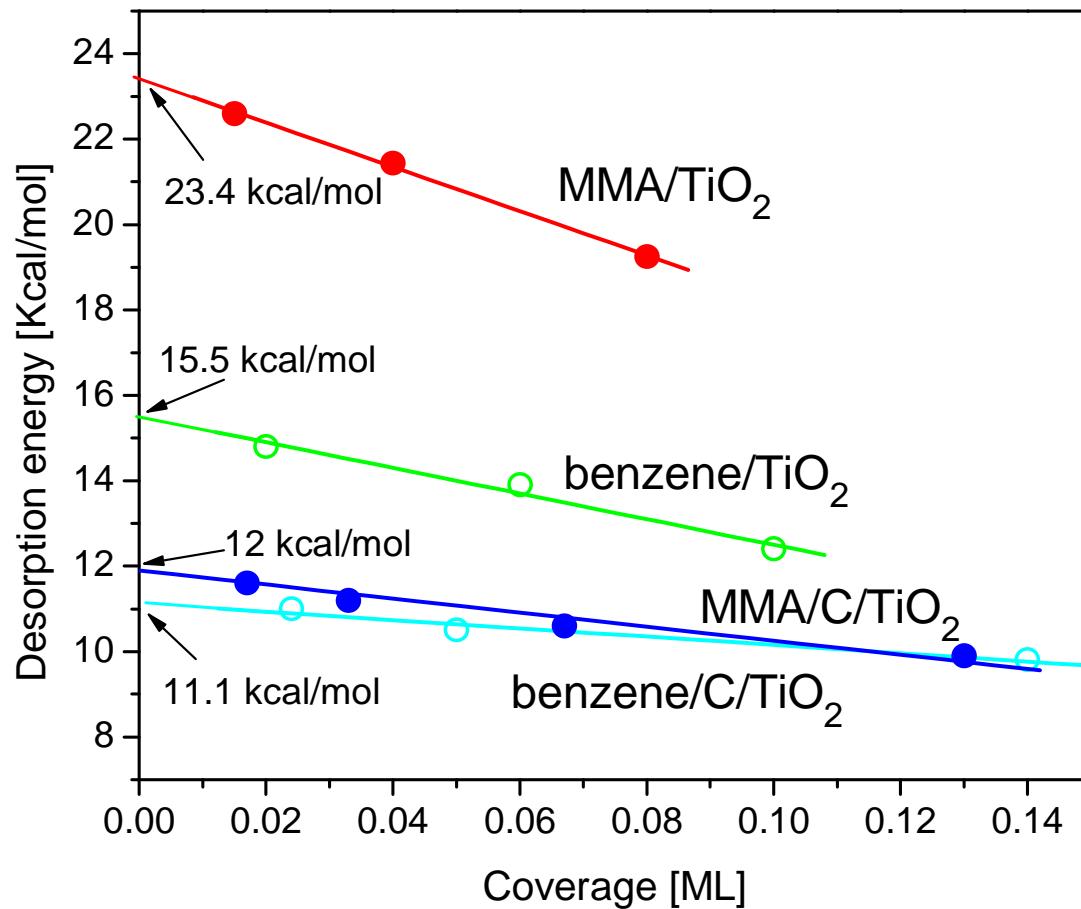
benzene



- Adsorption energy decreases with increasing coverage
- No carbon accumulation, reversible desorption

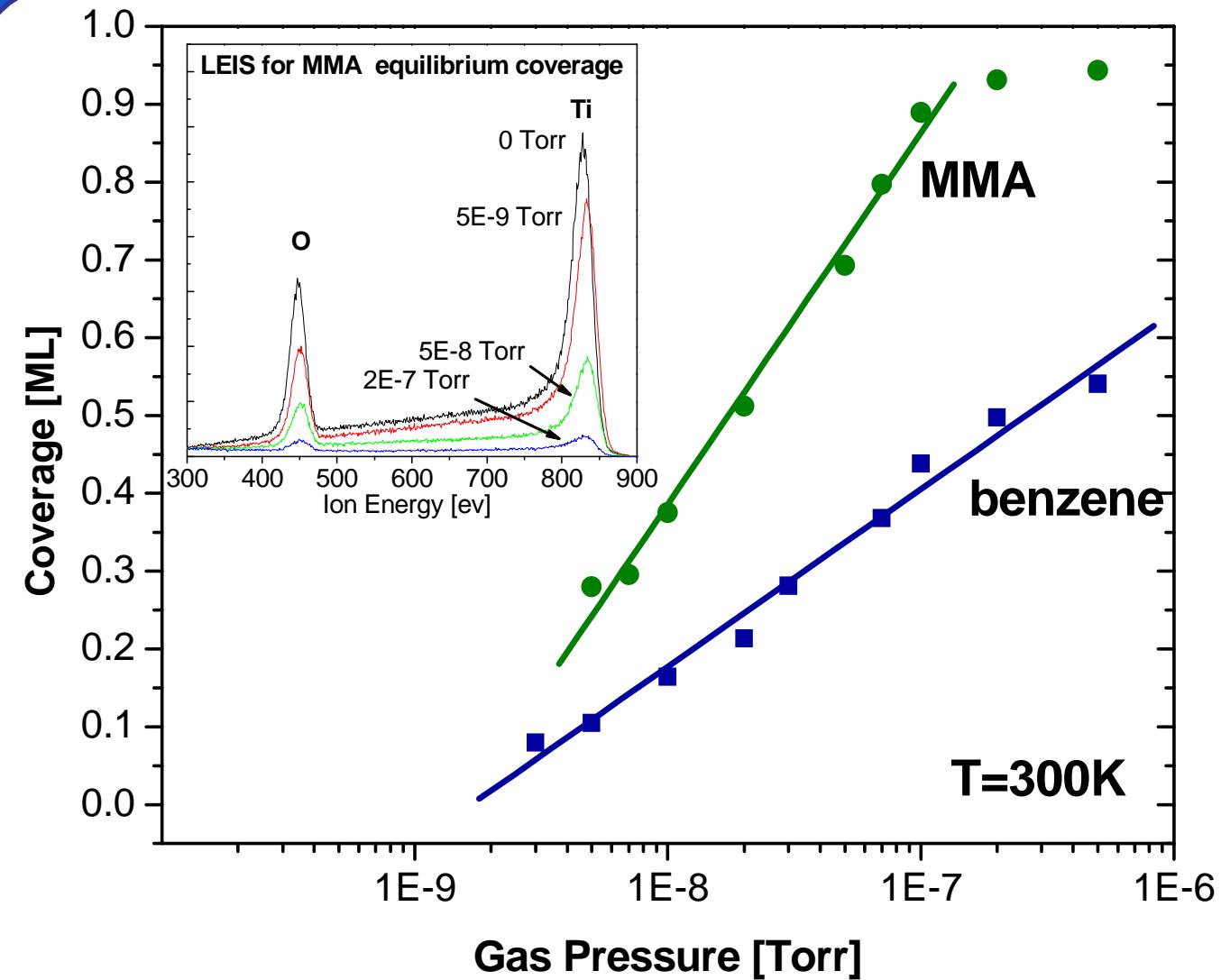


Adsorption energy of MMA and benzene, extrapolated to zero coverage



The data are extracted from TPD spectra
assuming the 1st order desorption

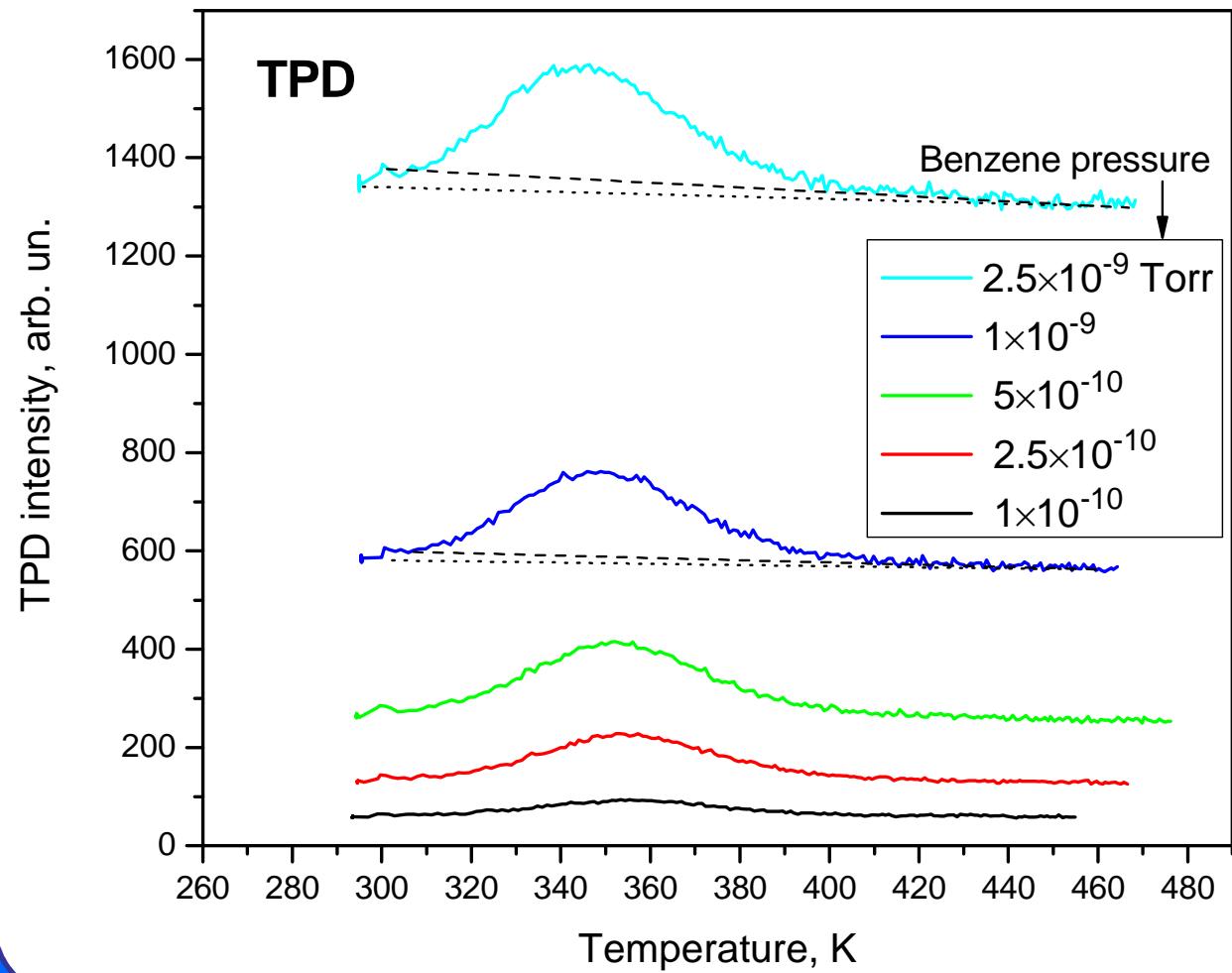
Steady-state benzene and MMA coverage



LEIS measurements.
Coverage depends on Log p

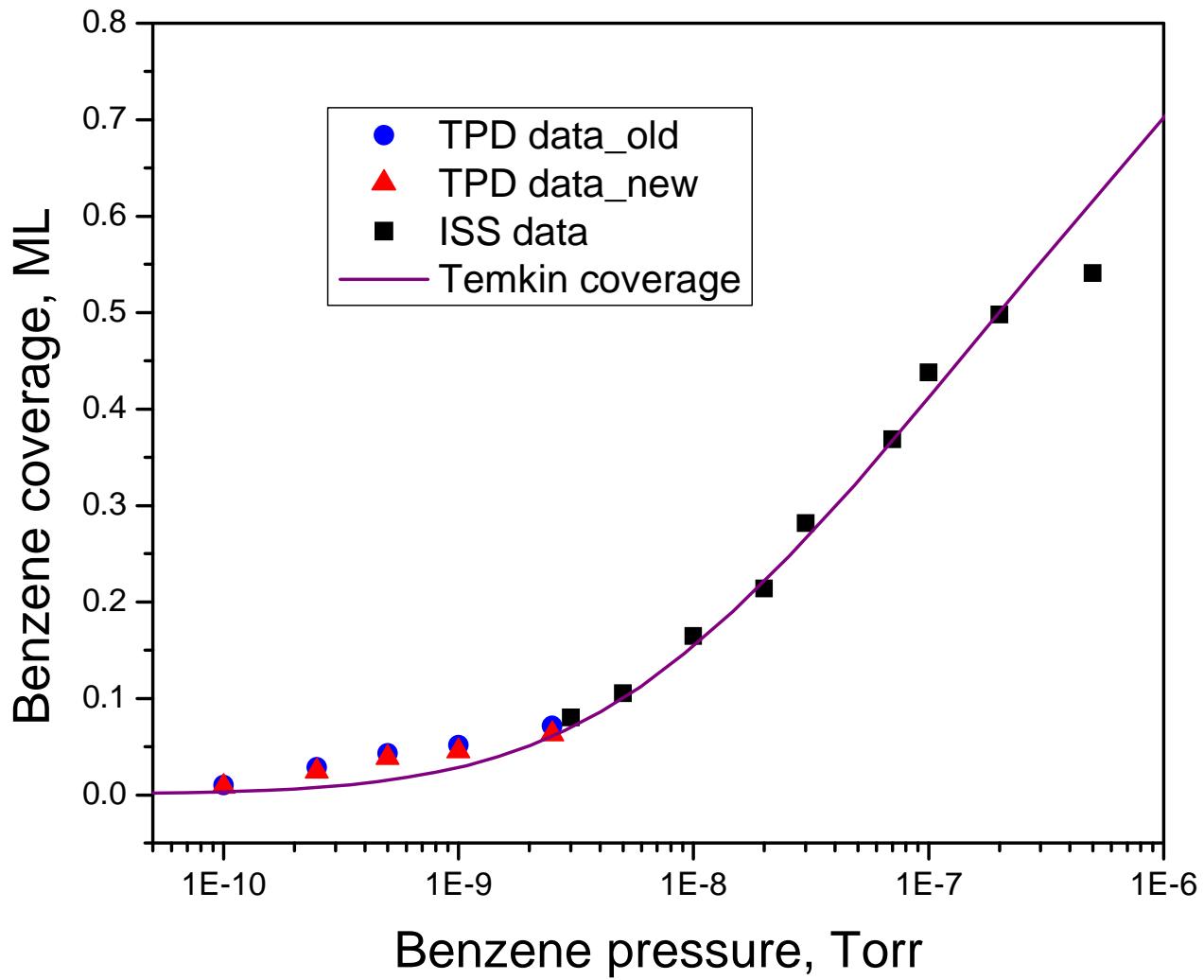
Estimation of steady-state benzene / TiO_2 coverage by TPD for low pressure range

Benzene/ TiO_2 steady-state coverage measurements by TPD. Raw data.



TPD feature rides on large background subtraction

Steady-state benzene / TiO_2 coverage

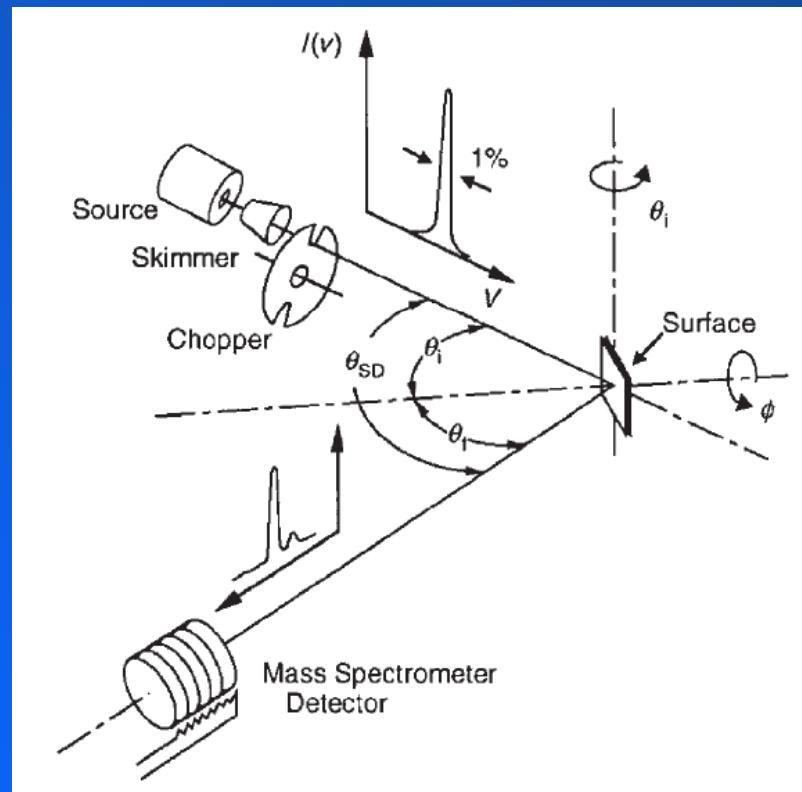


LEIS and TPD control. Coverage depends on Log p



He Atom Scattering

Highly sensitive to low adsorbate coverages

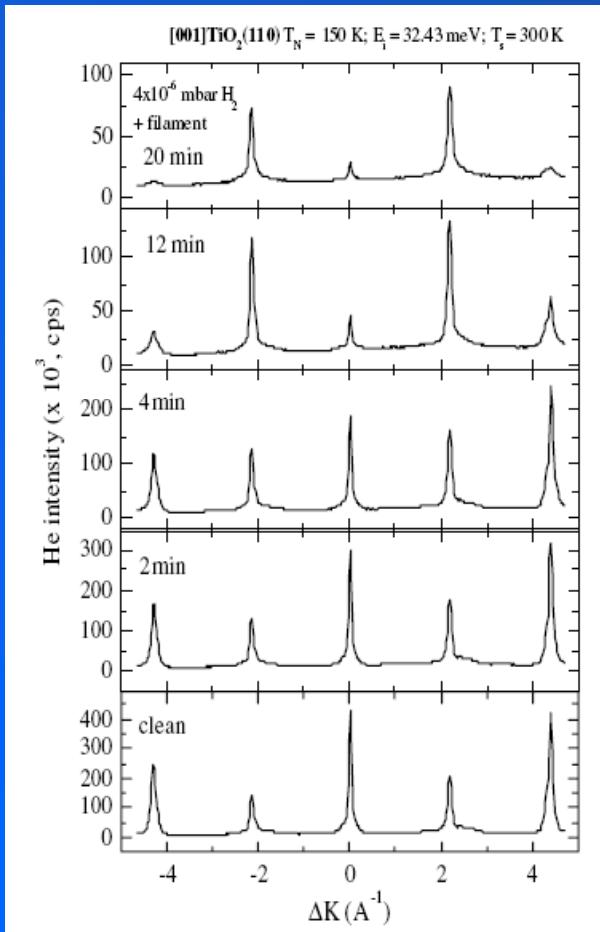


Traeger, Chem. Phys. Chem. 7, 1006 (2006)

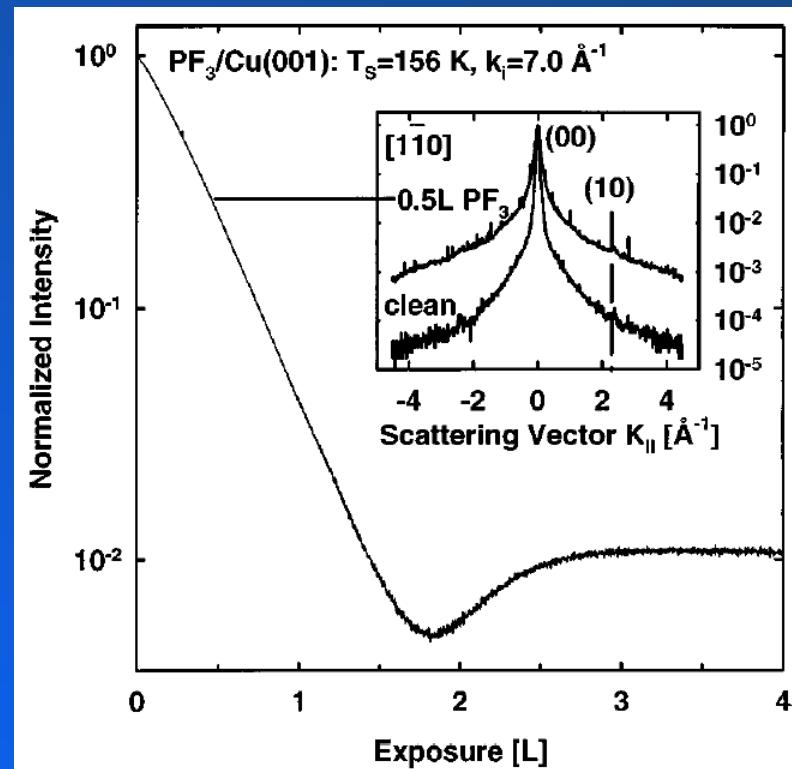


He Atom Scattering

H/TiO₂(110)



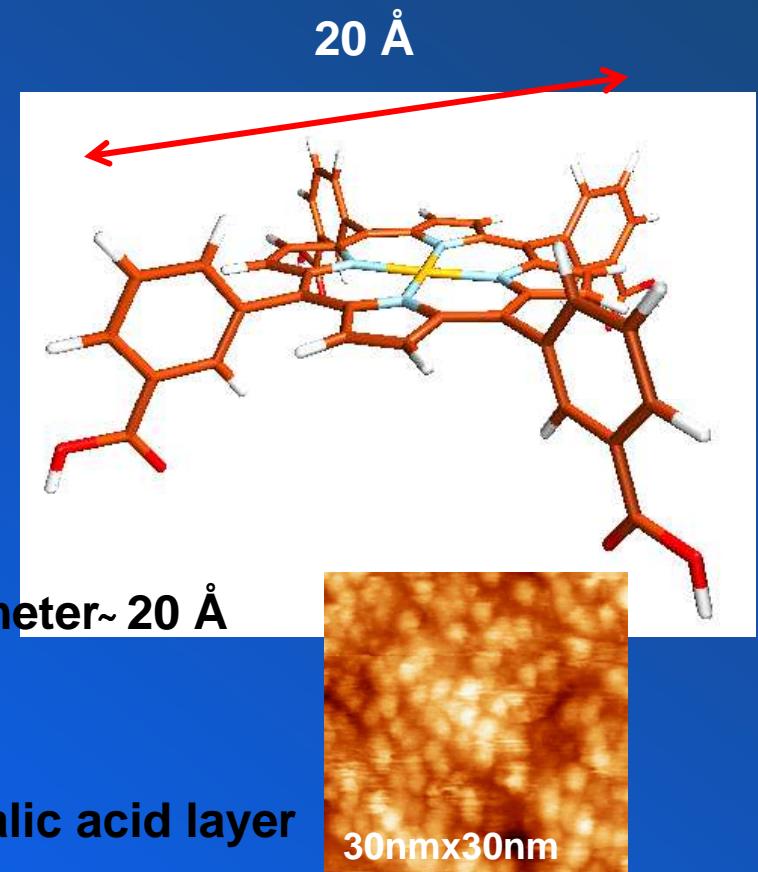
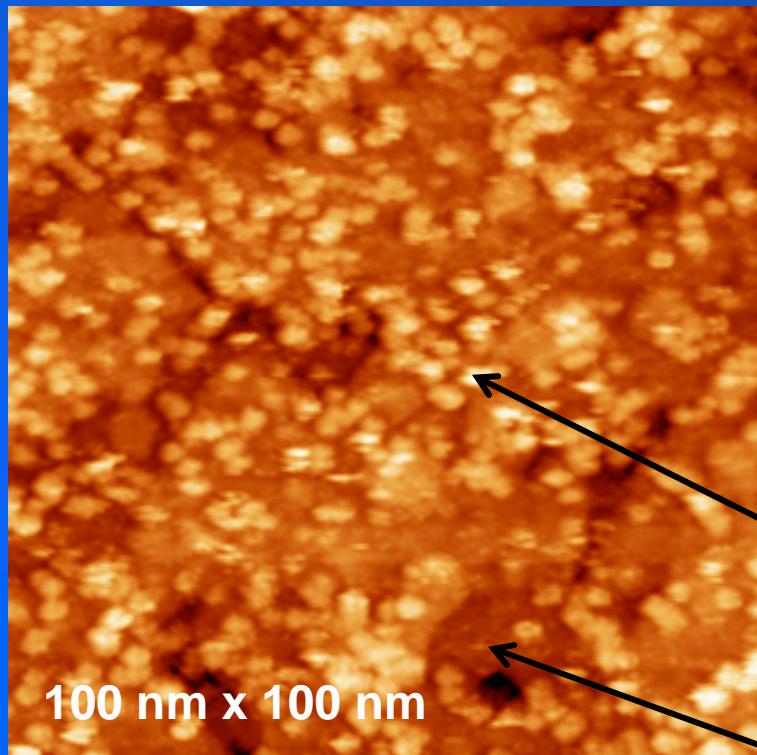
PF₃/Cu(100)



Hinch (Rutgers University)

Ch. Wöll, J. Phys: Condens. Matter 16, S2981 (2004)

ZnTPP derivative on $\text{TiO}_2(110)$





Summary

- Initial radiation-induced C-accumulation rate is substrate dependent.
- Limiting growth rates ~ same on TiO_2 , and Al_2O_3 for C thickness > 1 to 1.5 nm
- Electron energies as low as 20eV cause C-growth on TiO_2 → secondaries important
- Steady state coverage on TiO_2 and C/ TiO_2 go as $\log P$ → Temkin isotherms
- Steady state coverage measurements difficult for low P
 - Helium atom scattering?
 - STM?
 - Attaining ultralow pressure environment?



